NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2446

WIDTH OF DEBYE-SCHERRER LINES FOR FINITE SPECTRAL WIDTH OF PRIMARY BEAM

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SUMMARY

The width of a Debye-Scherrer line under the combined influence of spectral width of the primary radiation and of the small size of the crystal grains is calculated, omitting all geometric causes of line broadening. The shape of the crystals is assumed spherical, with the same diameter for all grains. The orientation is assumed to be random, with negligible statistical fluctuations. It is shown that the width under these circumstances is the sum of that width which is obtained with very large crystals ("spectral" width) and that which is obtained with monochromatic radiation ("size" width).

INTRODUCTION

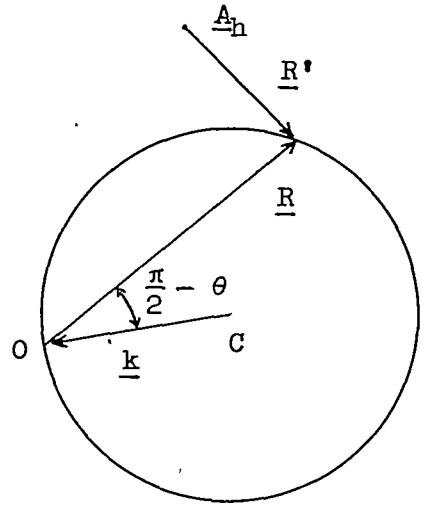
In 1926, Laue (reference 1) calculated the angular width of a beam diffracted by a uniformly random mass of crystals of uniform size and shape when it is irradiated by a parallel monochromatic beam. The physical problem is somewhat ill-defined, since the shape of the individual crystals is evidently widely different. However, the fact that experimental measurements are quite reproducible supports the assumption of a reasonable shape common to all crystals. Various workers have since then used different shapes and different approximation methods. Patterson (reference 2) derived a rigorous solution for the case of spherical shape for all crystals. Comparing this result with the approximate solution obtained by Laue's method, he concludes that one part of Laue's method (the tangent-plane approximation) is quite satisfactory, whereas the use of the approximation function is somewhat doubtful. Since the basic assumption of equal shape for all crystals is quite far from reality, it does not seem worth while to attempt high mathematical accuracy in calculating the form of the line. Laue's approximation method will be used in the following computations, and, for mathematical convenience, a spherical shape for the crystal grains will be assumed. In the previous papers, the reason for considering the monochromatic case only was the fact that the influence of the

actual spectral width of the characteristic radiation was considered negligible (reference 3). However, it has been shown (reference 4) that, for measurements of high precision, the influence of the spectral width, far from being negligible, becomes the decisive limiting factor. Consequently, it has become desirable to calculate the line width for the case of finite spectral width of the primary radiation. An investigation of this method of calculation was conducted at the Armour Research Foundation under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

This report is part of a cooperative project with Dr. Stanley Siegel.

CALCULATION OF INTENSITY DISTRIBUTION

Consider first the diffraction of a monochromatic wave by a single crystal in a definite direction. In the usual representation in Fourier space, as shown in the following diagram, CO is the wave vector having the direction of the incident beam and length $1/\lambda$,



if λ is the wave length and O is the origin of the reference system. The intensity scattered in the direction of CR is then proportional to the value of the interference function $|\psi|^2$ at the point of radius vector $\underline{R}$, that is, the point where the diffracted wave vector intersects the Laue sphere. If a reciprocal lattice point $\underline{A}_h$ is close to the point $\underline{R}$, the interference function at $\underline{R}$ will be very nearly equal to the contribution of the lattice point $\underline{A}_h$ (reference 2). Since a spherical crystal is considered, this dominant term of the interference function will have spherical symmetry with respect to the lattice point $\underline{A}_h$. Therefore, the scattered intensity will be

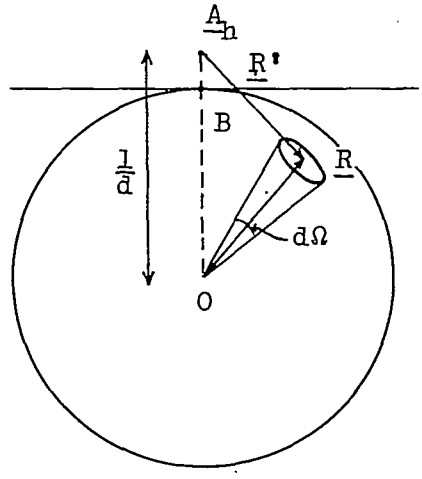
$$J_1 \propto |\psi(R')|^2 \tag{1}$$

that is, only a function of the length of the vector $\underline{R}'$ which joins the points $\underline{A}_h$ and $\underline{R}$.

In order to find the intensity diffracted by a mass of randomly oriented crystals of equal shape, the reciprocal lattice, that is, the point $\underline{A}_h$, might be rotated about O, the points C and $\underline{R}$ being fixed, and the intensity (equation (1)) integrated over all positions of the crystal. Alternatively, the triangle $CO\underline{R}$ might be rotated about O but with the point $\underline{A}_h$ fixed. Thus, the total intensity diffracted in the direction θ by the wave length $\lambda = 1/k$ is

$$J_2 \propto \int |\psi(R')|^2 \, d\Omega \tag{2}$$

where Ω is the solid angle about O (as shown in the following diagram).



If the spectral intensity distribution is given by a function f(k), the total intensity contributed by all wave lengths is

$$J \propto \iint |\psi(R')|^2 f(k) \, d\Omega \, dk \tag{3}$$

Since k and R are related by

$$R = 2k \sin \theta \tag{4}$$

equation (3) becomes:

$$J \propto \frac{1}{2 \sin \theta} \int f\frac{(R)}{R^2} \, dR \int |\psi(R')|^2 R^2 \, d\Omega \tag{5}$$

The exact expression for $|\psi|^2$ is too unwieldy for analytical purposes. In its place the approximation function

$$|\psi|^2 \approx \frac{\rho^2}{\left(R^2 + \frac{1}{\omega^2}\right)^2} \tag{6}$$

is used, following Laue's method, where ρ is the radius of the crystal. The constant ω is determined so that the ratio of space integral to maximum value becomes identical for the exact function and the approximation, equation (6). According to Patterson (reference 2), and using the above notation

$$\omega = \pi\rho \sqrt[3]{4/3} = 3.45\rho \tag{7}$$

The spectral distribution of energy near a characteristic line is given with sufficient approximation by an expression of the type

$$f(k) = \frac{A}{\left(k - k_o\right)^2 + B^2} \tag{8}$$

where A and B are constants.

This must be compared with the form in which the intensity function in its dependence upon λ is usually given; namely,

$$\frac{dJ}{d\lambda} = \frac{C}{\left(\lambda - \lambda_o\right)^2 + \left(\frac{w}{2}\right)^2} \tag{9}$$

where w is the half-width of the line, or

$$f(k) \approx \frac{dJ}{dk} = \frac{Ck_o^2}{(k - k_o)^2 + \left(\frac{k\, k_o w}{2}\right)^2} \tag{10}$$

Comparison with equation (8) shows that the variable k in the second term of the denominator should be replaced by k_o. Therefore,

$$f(k) = \frac{A}{(k - k_o)^2 + \left(\frac{k_o^2 w}{2}\right)^2} \tag{11}$$

Returning to equations (5) and (6), it is necessary to perform first the integration

$$\int \rho^2 \frac{R^2\, d\Omega}{\left(R^2 + \frac{1}{\omega^2}\right)^2} \tag{12}$$

over the surface of a sphere of radius R. Replacing, as usual, the sphere by its tangent plane normal to OA_h (see preceding diagram),

$$\rho^2 \int \frac{R^2\, d\Omega}{\left(R^2 + \frac{1}{\omega^2}\right)^2} \propto \rho^2 \int_0^{\infty} \int_0^{2\pi} \frac{r\, dr\, d\varphi}{\left[(d - R)^2 + r^2 + \frac{1}{\omega^2}\right]^2} = \frac{\pi\rho^2}{\left(\frac{1}{d} - R\right)^2 + \frac{1}{\omega^2}} \tag{13}$$

where r is the distance between the point B and a point on the tangent plane, and the usual notation $OA_h = 1/d$ is used. By equations (4), (5), (11), and (13),

$$J \propto \int_0^{\infty} \frac{dk}{\left[(k - k_o)^2 + \left(\frac{k_o^2 w}{2}\right)^2\right]\left[\left(\frac{1}{d} - 2k \sin\theta\right)^2 + \frac{1}{\omega^2}\right] 4k^2 \sin^2\theta} \tag{14}$$

is obtained.

Since only the neighborhood of $k = k_o$ contributes substantially to the integral, the lower limit of integration may be taken to be $-\infty$ instead of 0. Thus,

$$J \propto \frac{1}{\sin^4 \theta} \int_{-\infty}^{\infty} \frac{dk}{\left[k^2 + \left(\frac{1}{2\omega \sin \theta}\right)^2\right]\left[\left(k + k_o - \frac{1}{2d \sin \theta}\right)^2 + \left(\frac{k_o^2 w}{2}\right)^2\right]} \tag{15}$$

an integral which can be calculated by elementary methods:

$$J \propto \left(\frac{\pi}{\sin^4 \theta}\right)\left\{\frac{k_o^2 \frac{w}{2} + \frac{1}{2\omega \sin \theta}}{\frac{k_o^2 w}{4\omega \sin \theta}\left[\left(k_o - \frac{1}{2d \sin \theta}\right)^2 + \left(\frac{k_o^2 w}{2} + \frac{1}{2\omega \sin \theta}\right)^2\right]}\right\} \tag{16}$$

If

$$k_o w = \frac{w}{\lambda_o} = \alpha \tag{17}$$

$$\sin \theta = z \qquad \sin \theta_o = \frac{1}{2dk_o} = z_o \qquad z - z_o = \Delta z \tag{18}$$

$$\frac{1}{k_o \omega} = \frac{\lambda_o}{3.45\rho} = \beta \tag{19}$$

Equation (16) becomes

$$J \propto \frac{\alpha + \frac{\beta}{z}}{z^3 k_o^3 \alpha\beta\left[\left(\frac{\Delta z}{z}\right)^2 + \frac{1}{4}\left(\alpha + \frac{\beta}{z}\right)^2\right]} \tag{20}$$

Since $z = \sin \theta$ varies little over the width of the line, z_o may be written for z in equation (20). The intensity then becomes:

$$J \propto \frac{1}{(\Delta \sin \theta)^2 + \left(\frac{\sin^2 \theta_o}{2}\right)^2\left(\frac{w}{\lambda_o} + \frac{\lambda_o}{3.45\rho \sin \theta_o}\right)^2} \tag{21}$$

If θ is not too close to $\pi/2$, the following can be used:

$$\Delta \sin \theta = \cos \theta \, \Delta\theta = \frac{1}{2} \cos \frac{\Phi}{2} \Delta\Phi \tag{22}$$

where the deviation angle

$$\Phi = 2\theta \tag{23}$$

is used. The intensity becomes:

$$J \propto \frac{1}{(\Delta\Phi)^2 + \tan^2 \frac{\Phi}{2}\left(\frac{w}{\lambda_o} + \frac{\lambda_o}{3.45\rho \sin \Phi/2}\right)^2} \tag{24}$$

The intensity distribution is described by a resonance curve with the half-width

$$W = \frac{2w}{\lambda_o} \tan \frac{\Phi}{2} + \frac{0.58\lambda_o}{\rho \cos \Phi/2} \tag{25}$$

The first term is due to the spectral width alone; the second is due to the finite particle size alone. If the "integral breadth"

$$B = \frac{\int_{-\infty}^{\infty} J(\Phi) \, d\Phi}{J(\Phi)} \tag{26}$$

is used to characterize the line shape, the additivity expressed in equation (25) is also conserved. Indeed,

$$B = \frac{2\pi/W}{(2/W)^2} = \frac{\pi}{2}\left(\frac{2w}{\lambda_o} \tan \frac{\Phi}{2} + \frac{0.58\lambda_o}{\rho \cos \Phi/2}\right) \tag{27}$$

DISCUSSION

The half-value angular width of a line obtained by plane-parallel characteristic radiation on a target of a uniform mass of crystals is the sum of two terms: The "spectral" width which results for very large

crystals; and the "size" term which is obtained by a monochromatic radiation impinging upon crystals of finite size. The additivity of the widths is not obvious.

In Jones' semiempirical calculations, the breadth is not the sum of the "size" term and another term, independent of size, but the relation is complicated. The simple nature of the results presented herein is due to the omission of "geometric" broadening effects. However, these results have physical significance, because the geometric width can be reduced to a negligible quantity, if the time of exposure can be increased. In previous experiments (reference 4), the geometric factors were, in fact, small as compared with other factors.

Many authors (reference 5) propose for the line breadth a formula of the type

$$B = \sqrt{b_1^2 + b_2^2}$$

where b_1 is the size term and b_2 the breadth of a line obtained with very large crystals, this breadth being caused by all factors, geometrical and spectral. It appears that at least for negligible geometric width, this formula is not correct.

It is interesting to note that the ratio of the two terms in equations (25) or (27) is a function of the diffraction angle, namely, proportional to $\sin \Phi/2$. This means that the effect of the spectral width is negligible for small diffraction angles, whereas it tends to have the same effect as size broadening for back-reflection.

In conclusion, the considerations of previous work (reference 1) remain valid for crystals of finite size, provided that the size term is added to the spectral term of the line width.

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